

# Catalyst Screening for Single-Stage Catalytic Hydro-processing of Bio-oil in a Continuous Packed-bed Reactor for the Production of Hydrocarbon Fuel

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**Abstract-Bio-oils are not directly applicable as transportation fuels due to the presence of oxygenated components in their composition. The objective of this study was to test several catalysts to produce organic fractions from single-stage hydro-processing of bio-oil in a continuous packed-bed reactor. Six catalysts, four different reduced catalysts (Ni/Si-Al, CoMo/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, NiW/Si-Al, FeW/Si-Al) and two sulfided catalysts (CoMo/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> and NiMo/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>) were tested. A range of process parameters including temperatures ranging from 375-400 °C, 1000 psig hydrogen pressure, hydrogen flow rate of 500 ml/min and at a liquid hourly space velocity of 0.5 h<sup>-1</sup> were applied. The results from sulfided catalytic experiments were superior in comparison to reduced catalysts. Sulfided CoMo/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst demonstrated the highest catalytic activity among the catalysts tested. Sulfided CoMo/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst produced an organic fraction having a higher heating value of 41.2 MJ/kg, acid value of 5.2 mg KOH/g oil, a total water content of 1.3% and the oxygen content was reduced from 54.7 wt% in the raw bio-oil to 4.0 wt% in the hydrocarbon fraction. The organic fraction obtained with the best performing catalyst (sulfided CoMo/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst) was also analyzed by detailed hydrocarbon analysis and simulated distillation analysis.**

**Index terms: Bio-oil, Distillation analysis, Biomass, Catalyst, Thermo-mechanical conversion.**

## I. INTRODUCTION

Biomass is an attractive feedstock for partial replacement of combusted fossil fuel for energy production [1-3]. Fossil fuels have been shown to release large amounts of CO<sub>2</sub> which have been proven to increase climate warming. Biomass is a renewable material which has a negligible content of sulfur, nitrogen and ash, and decreased carbon dioxide emissions [3-5].

Biomass can be treated in different ways to convert it into more valuable forms. These methods include physical conversion, biochemical conversion and thermal conversion. The various routes of biomass thermochemical conversion processes are usually classified into combustion, gasification, liquefaction, hydrogenation and pyrolysis processes [6,7]. Among these processes pyrolysis has received special attention as it directly converts the biomass into solid, liquid and gaseous products by thermal decomposition, performed in the absence of oxygen. Fast pyrolysis of biomass produces a liquid termed pyrolysis oil which is usually referred to as bio-oil. Bio-oil is dark brown in color with a smoky odor. The yield of bio-oil obtained from fast pyrolysis typically ranges from 60 to 75 dry

wt% of wood depending on feedstock composition, process type and conditions [8].

Bio-oils are dark brown liquids that are composed of a mixture of numerous chemical compounds. Bio-oils contain approximately 10-15% organic acids, 10-20% aldehydes, 1-4% furfurals, 1-5% ketones, 2-5% alcohols, 5-10% carbohydrates, 2-5% phenolics, 15-30% water insoluble lignin fragments and 20-30% water [9].

Raw bio-oil has been test combusted in diesel engines, both neat and as emulsions containing petroleum fuels or as diesel fuels in which bio-oil is fed in to the engine simultaneously with a fossil fuel. Raw bio-oil has also been tested in turbines and Stirling engines for the production of electricity. With the exception of the Stirling engine test researchers detected engine corrosion, deposits and significant wear [10]. While there was no damage to the Stirling engine the electrical generation efficiency was low. It is currently universally agreed that bio-oils must be upgraded prior to their utilization as engine fuels [8,11, 12].

Currently tested upgrading techniques include hydrodeoxygenation (HDO) [13-17], catalytic cracking of pyrolysis vapours [18], steam reforming [19,20], emulsification [21], chemical extraction, esterification [22,23] and olefination [24-26]. Other studies that involve removal of oxygen in the form of CO or CO<sub>2</sub> are by decarbonylation and decarboxylation reactions by thermal or catalytic processes [27]. However, complete oxygen removal was not achieved with these techniques. Several studies have been reported on oxygen removal from oxygenated model compounds with catalysts other than conventional sulfided catalysts [22,28-31].

Well known catalysts that have been tested for the hydrotreatment of pyrolysis oil include conventional hydrodesulfurisation catalysts such as sulfided CoMo/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, NiMo/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, and NiMo/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub> [32,33]. Elliot et al. developed a two-step hydrotreating process for upgrading of pyrolysis oil which was characterized by a low temperature mild hydrotreating step, performed at a temperature of 270 °C and 13.6 MPa pressure to avoid polymerization of oxygen-containing compounds, catalyst coking and reactor plugging. This hydrotreating step was then followed by a higher temperature hydrocracking step performed at 400 °C and 13.6 MPa pressure to remove oxygen in presence of the sulfided (CoMo/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> and NiMo/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>) catalysts. This process of

low temperature hydrotreating followed by hydrocracking is now widely used by many HDO practitioners [11,34-40].

The relatively higher activity of sulfided CoMo or NiMo/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> can be attributed to the formation of the active Co(Ni)MoS phase, consisting of highly dispersed MoS<sub>2</sub> crystallites coated with Co or Ni atoms that act as promoters when the oxide form is subjected to the sulfidation process [38,40].

From the above studies researchers concluded that the bio-oils obtained by fast pyrolysis of biomass may be converted to hydrocarbons that have the potential to serve as an alternative source for transportation fuels. However, rapid catalyst deactivation and low yields continue to be drawbacks in the HDO process. Therefore, further research is required to optimize the current HDO methods and catalysts.

The present study focused on testing various catalysts for the direct hydroprocessing of bio-oil in a continuous packed-bed reactor. Six different catalysts were screened. These catalysts included four reduced catalysts (Ni/Si-Al, NiW/Si-Al, FeW/Si-Al and CoMo/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>) and two sulfided catalysts (CoMo/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> and NiMo/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>).

## II. MATERIALS AND METHODS

### Materials

Bio-oil was produced by the fast pyrolysis process at a temperature of 400-450 °C under nitrogen gas atmosphere using a 7 kg/h auger-fed pyrolysis reactor located in the Department of Sustainable Bioproducts, Mississippi State University. The feedstock was loblolly pine ground to 1-3 mm and dried to 8% moisture content.

### Catalysts

Catalyst supports such as Si-Al,  $\gamma$ -alumina and the required inorganic metal salts for preparation of Ni/Si-Al (25% Ni), NiW/Si-Al (10% Ni, 5% W), FeW/Si-Al (5% Fe, 5% W) and NiMo/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> (5% Ni, 15% Mo) catalysts, were commercially purchased from Alfa Aesar, Sigma Aldrich and Fisher Scientific. The Ni/Si-Al, NiMo/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, NiW/Si-Al, and FeW/Si-Al catalysts were prepared by the wet-impregnation method. In impregnation process, the metal salts were impregnated on catalyst supports and then dried at 120 °C for 4-6 h before being calcined at 550 °C for 4 h. The calcined metal-dispersed catalysts were then reduced at 700 °C using hydrogen flow (100 ml/m) for 4 hr. CoMo/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> was purchased from Alfa Aesar. Cyclohexane and carbon disulfide (commercially available) were purchased from Fisher Scientific. The oxide form of catalysts were activated by subjecting them to a sulfidation process prior to the hydroprocessing experiments. CoMo/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> and NiMo/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> were sulfided with a solvent mixture of 2 vol% carbon disulfide and cyclohexane. To 800 ml of cyclohexane solvent, 16 ml (2 vol%) of carbon disulfide was added and the solvent mixture was pumped through a high-pressure dual-pump system. Catalyst sulfiding was performed at

300 °C, a pressure of 750 psi and LHSV of 1 h<sup>-1</sup> for a period of 4 h.

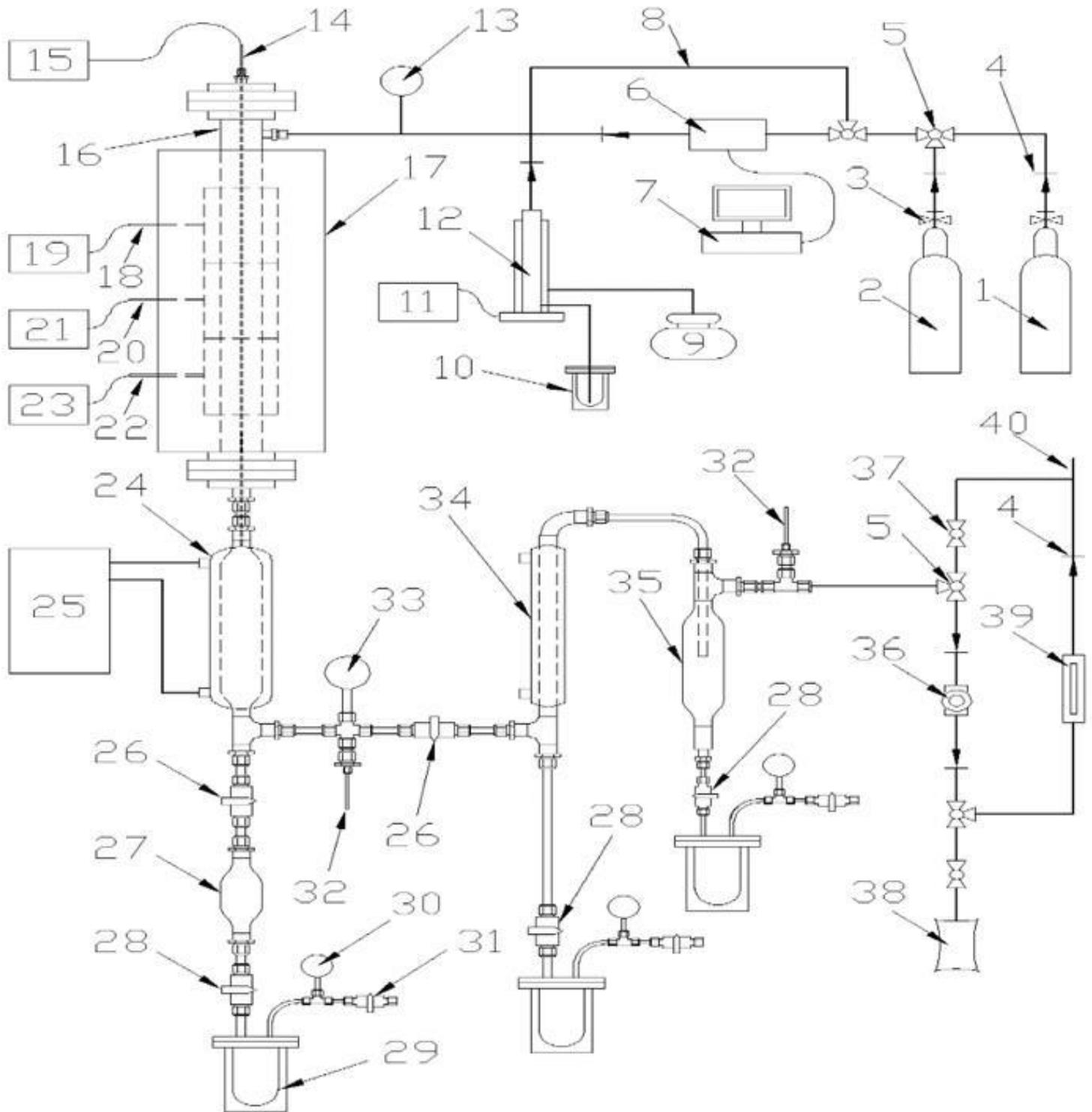
### Continuous packed-bed reactor

The continuous packed-bed reactor (**Figure 1**) used in the experiments consisted of a 1" I.D tubular reactor enclosed in a three-zone electric furnace (three 6" zones each independently controlled by its own temperature controller) followed by a condensation system. The temperatures inside the reactor were monitored with a point profile thermocouple equipped with ten sensing points (Omega Instruments). Three temperature sensing points were located in each of the 3 reactor heater zones for a total of 9. The tenth temperature sensing point was located at the condenser orifice. The catalyst bed temperature zones were maintained as closely as possible to the desired temperature set point through the course of the experiment. The catalytic reaction is exothermic such that temperatures are difficult to control due to the adiabatic nature of the reaction. Temperature controlled within a temperature range of 375-400 °C was possible. The bio-oil was pumped into the catalyst tube with a high-pressure dual-pump system (Teledyne Isco 500D). The hydrogen flow rate was controlled with a mass flow controller (MFC; Brooks Instruments), and the reactor pressure was controlled with a back-pressure regulator.

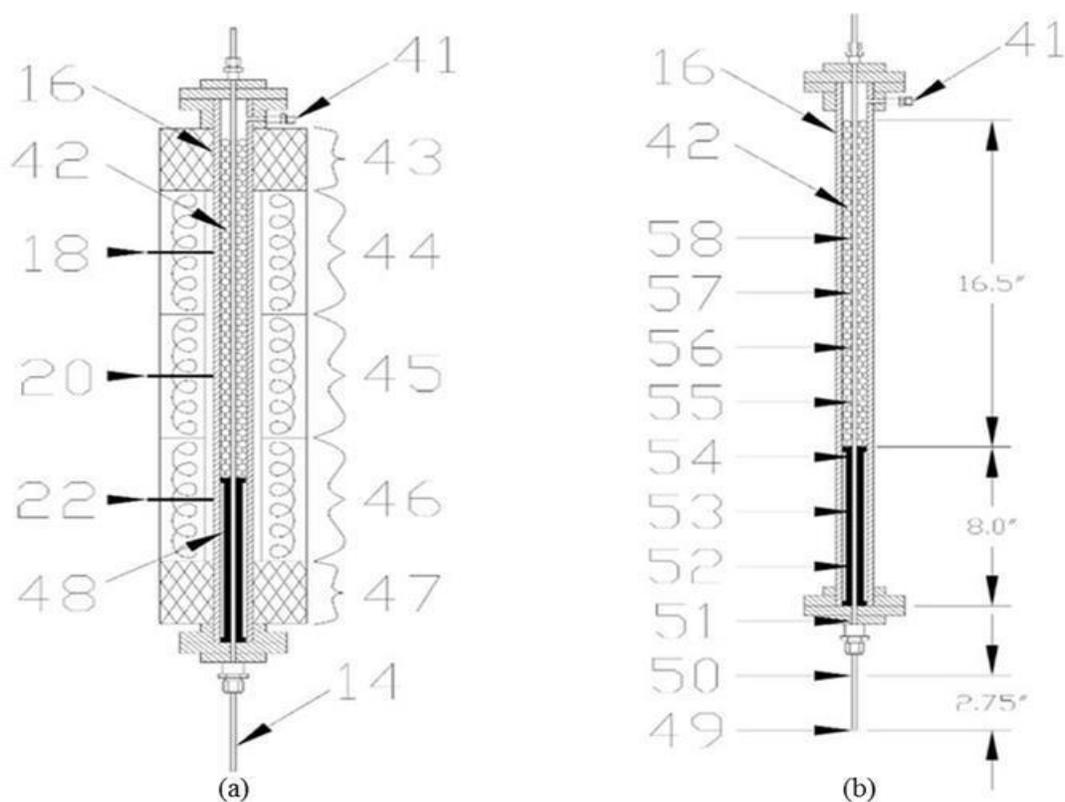
**Figure 1** shows a diagram of the schematic of the continuous packed-bed reactor. **Figure 2a and b** shows the method of catalyst loading in the continuous packed-bed reactor (a. Method of catalyst loading inside the reactor, enclosed in a furnace; b. Inside reactor with loaded catalyst).

For all experiments the reactor was loaded with catalyst at a temperature initially set to 150 °C. Once this initial temperature set point was attained, the reactor temperature was raised by another 100 °C; upon reaching the resultant temperature of 250 °C, the reactor temperature was again raised to 350 °C. A final 25 to 50 °C increase was often applied to raise the actual reaction temperature as close to 375 °C as possible. The reactor was pressurized to the desired 1000 psi hydrogen reaction pressure. After attaining the temperature of approximately 375 °C, the desired hydrogen pressure of 1000 psi was supplied to the reactor by a mass flow controller (MFC) producing a desired flow rate of 500 ml/min.

All experiments were performed at a LHSV of 0.5 h<sup>-1</sup>. The exit gas flow rate in milliliters per minute (ml/min) was monitored by an Agilent gas flow meter. Products exiting from the packed-bed reactor were cooled in the condenser and the liquid products were collected in a sampling bottle at 2 h intervals. Periodic gas sampling was also performed every 2 h using Tedlar sampling bags. The experiments were performed over a period of 4 h. The collected liquid products were centrifuged for 1 h to separate the aqueous fraction (AF) and organic fraction (OF). **Table 1** describes the numbered components of the continuous packed-bed reactor provided in **Figure 1**, and **Figure 2a and b**.



**Figure 1.** Schematic of the continuous packed-bed reactor.



**Figure 2a and 2b.** Method of catalyst loading in continuous packed-bed reactor. (a. Method of catalyst loading inside the reactor, enclosed in a furnace; b. Inside reactor with loaded catalyst)

**Table 1.** The numbered components of the continuous packed-bed reactor corresponding to **Figure 1** and **Figure 2** labels.

1	Hydrogen cylinder	30	Sampling vessel pressure gauge
2	Air cylinder	31	Sampling vessel ball valve
3	Cylinder regulator	32	Thermocouple
4	Check valve	33	Reactor exit pressure gauge
5	Three-way valve	34	Condenser 2
6	Mass flow controller (MFC)	35	Condenser 3
7	Computer-MFC program	36	Back pressure regulator
8	MFC bypass line	37	Needle valve
9	Air compressor	38	Gas sample bag
10	Bio-oil	39	Exit gas flow meter
11	High pressure pump controller	40	Gas exit line
12	High pressure pump	41	Bio-oil inlet

13	Reactor inlet pressure gauge	42	Catalyst
14	Ten zone reactor thermocouple	43	Heater top insulation, 3" long
15	Ten zone thermocouple monitor	44	Heater zone 1, 6" long
16	Reactor tube	45	Heater zone 2, 6" long
17	Reactor tube heater	46	Heater zone 3, 6" long
18	Heater zone 1 thermocouple	47	Heater bottom insulation, 3" long
19	Heater zone 1 controller	48	Catalyst support
20	Heater zone 2 thermocouple	49	Reactor thermocouple zone 1
21	Heater zone 2 controller	50	Reactor thermocouple zone 2
22	Heater zone 3 thermocouple	51	Reactor thermocouple zone 3
23	Heater zone 3 controller	52	Reactor thermocouple zone 4
24	Condenser 1	53	Reactor thermocouple zone 5
25	Chiller	54	Reactor thermocouple zone 6
26	Ball valve	55	Reactor thermocouple zone 7
27	Hydrocarbons storage vessel	56	Reactor thermocouple zone 8
28	Needle valve	57	Reactor thermocouple zone 9
29	Sampling vessel	58	Reactor thermocouple zone 10

#### **Physical and chemical analysis**

Raw bio-oil (RBO) and the organic fraction (OF) produced from the hydroprocessing treatments were characterized following ASTM methods. For the acid value (AV) test, 1 g of sample was dissolved in isopropanol/water (v/v =35:65) solution and then titrated with 0.1 N NaOH to a pH of 8.5. The AV was then calculated as the required milligrams (mg) amount of NaOH equivalent to 1 g of sample, according to ASTM D664 [41,42]. The higher heating value (HHV) was determined with a Parr 6400 automatic isoperibol calorimeter according to ASTM D240. The Karl Fischer method was employed to determine water content (WC) by ASTM E203 with a Cole-Parmer Model C-25800-10 titration apparatus. Elemental analysis (CHNO) for determination of percent carbon (C), percent hydrogen (H), percent nitrogen (N) and percent oxygen (O) were determined by EAI CE-440 elemental analyzer, with oxygen content determined by difference by the ASTM D5291 method. Based on the significantly superior performance of the catalyst, one best-performing catalyst (based on properties and yields) was chosen for more detailed analysis. Product analysis was by detailed hydrocarbon analysis (DHA) and simulated distillation (SIMDIS). DHA was performed by a PerkinElmer Clarus 680 GC equipped with a built-in model Arnel 4060 DHA analyzer, performed by ASTM D6730-01 method. SIMDIS was performed by the ASTM D2887 method on a gas chromatograph.

#### **III. EXPERIMENTAL DESIGN**

Each experiment was performed in triplicate. A factorial arrangement of treatments in a completely randomized design was employed with the one factorial being catalyst type. The statistical analysis was performed with SAS software version 9.3. The analysis of variance (ANOVA) model as shown in Eq.1 was comprised of one factorial with six catalyst levels, four reduced and two sulfided catalysts (Ni/Si-Al, NiW/Si-Al, FeW/Si-Al, CoMo/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, sulfided (CoMo/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> and NiMo/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>) catalysts to determine their influence on physical properties of AV, HHV, oxygen content and WC. ANOVA Eq. 1 was also applied to yield analysis.

All study statistical tests were performed at the 0.05 level of significance. The ANOVA results showed that the main effect of catalyst type treatments was significant at the 0.05 level of significance for all physical properties as well as yields, satisfying the requirement of Fisher's protected LSD [43]. The least significant difference (LSD) test was performed to separate the physical property means as influenced by the catalyst treatments.

The ANOVA model was performed for each of the physical properties and liquid yields.

$$Y_i = \beta_0 + \beta_1 A_i + e_i$$

Where:

$Y_i$  represents dependent variable physical or chemical testing values: acid value,

HHV, Oxygen percent, WC and yields,

$\beta_0$  represents the intercept term,

$\beta_1 A_i$  represents the influence of catalyst type ((Ni/Si-Al, NiW/Si-Al, FeW/Si-Al, CoMo/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, sulfided CoMo/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> and NiMo/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>)

$e_i$  represents the random error term.

The efficacy of catalyst treatment means were compared by the LSD comparison of means method performed for each of the physical properties (AV, HHV, WC, oxygen content); yields (total yields (TY, AF and OF)) were also independently tested by the LSD method. The 3 replicate values of each catalytic treatment were included in the test to determine the influence of each catalyst on properties and yields.

#### IV. RESULTS AND CONDITIONS

##### Catalyst screening

Table 2 gives the mean values of the AV, HHV, oxygen percent, WC and yields to analyze the effect of catalyst type treatments (Ni/Si-Al, NiW/Si-Al, FeW/Si-Al, CoMo/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> and sulfided CoMo/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> and NiMo/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>). Letters in parentheses indicate significant differences between property means as influenced by catalyst type.

The mean AV for the reduced catalysts of Ni/Si-Al, NiW/Si-Al, FeW/Si-Al and CoMo/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> of the organic fractions (OF) decreased significantly from 95.9 to 44.7, 45.8, 42.4 and 18.8 mg KOH/g, respectively. Among the reduced catalysts, CoMo/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> AV was significantly lower than the other three reduced catalysts. These values are all approximately half of the AV of raw bio-oil. For the sulfided CoMo/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> and NiMo/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> the mean AV decreased significantly from 95.9 to 5.2 and 9.4 mg KOH/g, respectively. Among all tested catalysts (both reduced and sulfided catalysts), sulfided CoMo/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> had the significantly lowest AV of 5.2 mg KOH/g.

**Table 2.** Effect of catalyst on mean values for physical properties. AV, HHV, Oxygen content (%), WC (%). Letters in parentheses indicate significant differences between property means as influenced by catalyst type.

Catalyst	AV (mg KOH/g)	HHV (MJ/Kg)	Oxygen content (%)	WC (%)
Rawbio-oil (Control)	95.9 (a)	16.4 (g)	54.7 (a)	29.2 (a)
Ni/Si-Al	44.7 (c)	35.9 (d)	14.2 (d)	5.1 (b)
NiW/Si-Al	45.8 (b)	33.5 (f)	18.6 (b)	5.1 (b)
FeW/Si-Al	42.4 (d)	34.6 (e)	15.9 (c)	4.6 (c)
Reduced CoMo/ $\gamma$ -Al <sub>2</sub> O <sub>3</sub>	18.8 (e)	37.9 (c)	11.5 (e)	4.0 (d)
Sulfided CoMo/ $\gamma$ -Al <sub>2</sub> O <sub>3</sub>	5.2 (g)	41.2 (a)	4.0 (g)	1.3 (f)
Sulfided NiMo/ $\gamma$ -Al <sub>2</sub> O <sub>3</sub>	9.4 (f)	39.4 (b)	7.0 (f)	2.0 (e)

The mean HHV of the OF of reduced catalysts for Ni/Si-Al, NiW/Si-Al, FeW/Si-Al and CoMo/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> were increased from 16.4 for raw bio-oil to 35.9, 33.5, 34.6 and 37.9 MJ/Kg, respectively. The HHV's of Ni/Si-Al, NiW/Si-Al and FeW/Si-Al differed very little with each other. Among the reduced catalysts the CoMo/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> HHV was significantly higher than the other three reduced catalysts. In the case of the sulfided catalysts, the sulfided CoMo/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> and NiMo/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> had mean HHV's of 41.2 and 39.4 MJ/Kg respectively, which were significantly higher than the HHV of the control (16.4 MJ/Kg) as well as the other four reduced catalysts HHV (35.9, 33.5, 34.6 and 37.9 MJ/Kg). From the tested catalysts, sulfided CoMo/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst showed the highest HHV of 41.2 MJ/Kg,

followed by NiMo/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> with the second highest HHV of 39.4 MJ/Kg.

The mean oxygen content of OF for reduced catalysts of Ni/Si-Al, NiW/Si-Al, FeW/Si-Al and CoMo/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> was decreased significantly from 54.7 to, 14.2, 18.6, 15.9 and 11.5%, respectively. Among the reduced catalysts CoMo/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> performed the best in terms of oxygen content. For the sulfided catalysts CoMo/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> and NiMo/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> showed an oxygen content reduction from 54.7 to 4.0 and 7.0 %, respectively. The OF of the product obtained with sulfided CoMo/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst had significantly lower mean oxygen (4.0%) content followed by NiMo/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst with the significantly next lowest oxygen content (7.0%).

The mean WC percentages of OF for Ni/Si-Al, NiW/Si-Al, FeW/Si-Al and CoMo/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalysts were decreased from that of the control at 29.2% to 5.1, 5.1, 4.6 and 4.0%, respectively. The statistical results show that, the WC content of the OF did not differ significantly between the Ni/Si-Al and NiW/Si-Al reduced catalysts. The sulfided catalysts CoMo/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> and NiMo/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, had WC percentage values of 1.3 and 2.0. The WC percentage for the sulfided catalysts CoMo/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> and NiMo/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> differed a little (0.7% difference), but the difference was significant. A comparison of results

for both the reduced and sulfided catalysts showed sulfided CoMo/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> had significantly superior performance in terms of WC reduction.

The yields (overall yields (TY), AF and OF) for hydroprocessing treatments are given in **Table 3**, with different letters given in brackets indicating a significant difference between each catalyst treatment mean.

**Table 3.** Effect of catalysts on yields (total liquid yields (TY), aqueous (AF) and organic fraction (OF)).

Catalyst	TY (wt%)	AF (wt%) yield	OF (wt%) yield
Ni/Si-Al	67.1 (d)	51.4 (f)	16.3 (d)
NiW/Si-Al	66.6 (e)	57.0 (e)	9.7 (f)
FeW/Si-Al	67.1 (d)	52.9 (d)	14.3 (e)
Reduced CoMo/ $\gamma$ -Al <sub>2</sub> O <sub>3</sub>	68.4 (c)	53.1 (c)	15.7 (c)
Sulfided CoMo/ $\gamma$ -Al <sub>2</sub> O <sub>3</sub>	85.3 (b)	58.2 (b)	27.0 (a)
Sulfided NiMo/ $\gamma$ -Al <sub>2</sub> O <sub>3</sub>	86.3 (a)	61.5 (a)	25.1 (b)

The mean TY yields for Ni/Si-Al, NiW/Si-Al, FeW/Si-Al and CoMo/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> were 67.1, 66.6, 67.1 and 68.4%, respectively. The mean TY yields of reduced Ni/Si-Al and FeW/Si-Al did not differ significantly. For the sulfided catalysts, CoMo/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> and NiMo/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> the TY's were 85.3 and 86.3% respectively. The mean AF yields for reduced Ni/Si-Al, NiW/Si-Al, were 51.4 and 57.0% and were significantly lower than the mean AF's of FeW/Si-Al (52.9%) and CoMo/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> (53.1%), respectively. For sulfided catalysts the mean AF yields were 58.2 and 61.5% respectively. Among all the catalysts reduced FeW/Si-Al and CoMo/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> had the significantly lowest AF yields. For reduced catalysts, Ni/Si-Al, NiW/Si-Al, FeW/Si-Al and CoMo/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> the mean OF yields were 16.3, 9.7, 14.3, and 15.7%, respectively, and each mean differed significantly. For the sulfided catalysts, CoMo/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> and NiMo/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, the OF yields were 27.0 and 25.1%, respectively. The sulfided catalysts, CoMo/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> and NiMo/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, had the significantly highest OF yields among the catalyst treatments tested. The sulfided CoMo/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst had the significantly highest OF yield. For best performing sulfided CoMo/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst, gas yields and char yields were calculated and are shown in Table 4.

Based on the results of OF yields and oxygen content we have determined that the sulfided CoMo/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst had the significantly highest

OF yield and lowest oxygen content. In terms of the remaining physical and chemical test results we observed that the sulfided CoMo/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst had the lowest AV, highest HHV, and lowest WC percentage. Therefore, the sulfided CoMo/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst performed the best compared to other study catalysts. The high activity of sulfided CoMo/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst was due to the formation of Co-Mo-S phase in the catalyst. Co-Mo-S phase is believed to be the active phase, and is formed by the intercalation of Co at the edges of MoS<sub>2</sub> surface. Based on the significantly superior performance of the sulfided CoMo/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst, it was chosen for more detailed analysis (DHA, SIMDIS and FTIR). For this one best performing sulfided CoMo catalyst showed best performance in terms of properties. The gas, char yields, hydrogen consumption are shown in **Table 4**.

**Table 3** shows the analysis of gas samples collected during the hydroprocessing experiments for sulfided CoMo/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst. Gas samples were collected prior to collecting the liquid samples. Gas analysis was used to interpret the exit gases. The exit gases from the experiment using sulfided CoMo/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst had 65.6% hydrogen, 0.2% oxygen, 0.5% nitrogen, 3.1% methane, 0.1% carbon monoxide, 8.1% carbon dioxide and 22.8% methane, respectively.

**Table3.** Gas analysis, hydrogen consumption and the hydrogen conversion for the hydroprocessed product (OF) of the sulfided CoMo/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst.

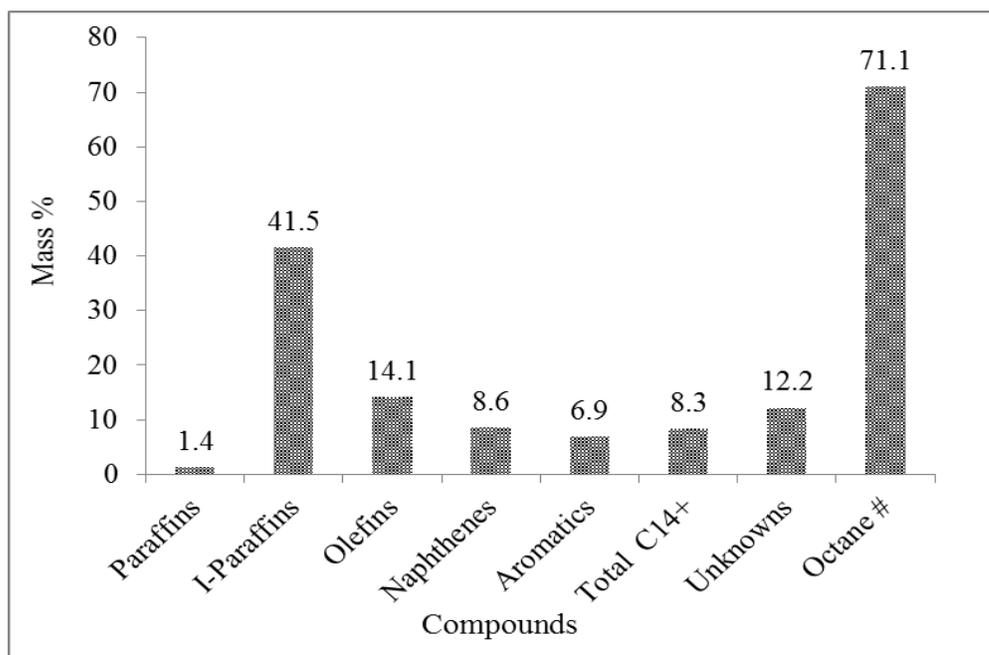
Gas	Units (mass%)
H	65.60%
O	0.20%
N	0.50%
CH <sub>4</sub>	3.10%
CO	0.10%
CO <sub>2</sub>	8.10%
C <sub>2</sub> H <sub>4</sub>	22.80%
Hydrogen consumption	203.2 ml/min
Yields (wt%)	Wt%
Gas yield	0.08 g/g feed or 8.7 wt%
Char yields	6.0 to 8.0 wt%

The hydrogen consumption for sulfided CoMo/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> was 203.2 ml/min. Higher hydrogen consumption indicates higher deoxygenation. Yields of hydroprocessed product including gas and char from the experiment using sulfided CoMo/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst were 0.08, g/g feed or 8.0 wt% and 6.0 to 8.0 wt% feed, respectively.

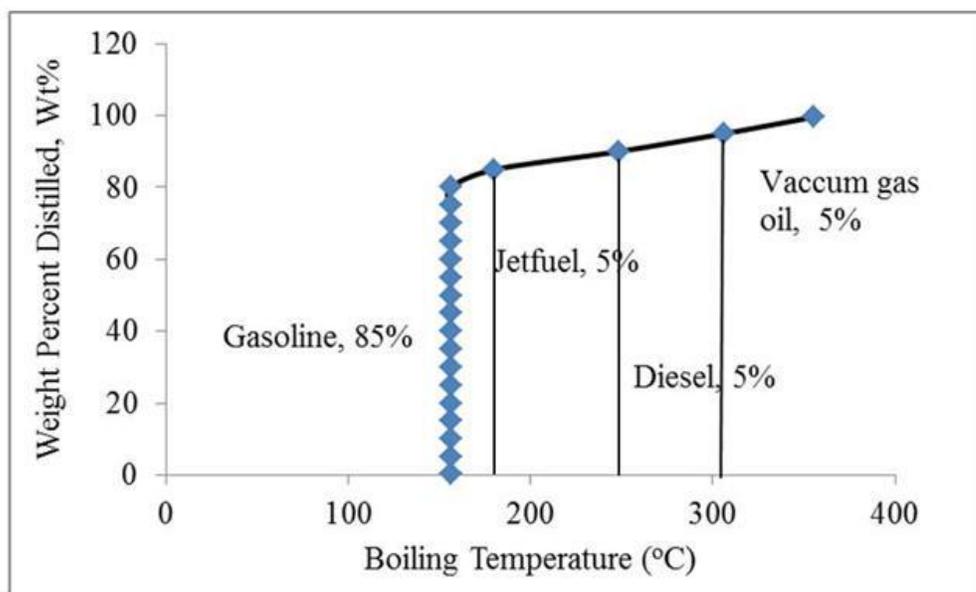
**Figure 3** shows the DHA of mixed liquid hydrocarbons obtained with reduced CoMo/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> and sulfided CoMo/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst, performed according to ASTM D6730-01. The DHA of the sulfided CoMo/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst upgraded product predominately contained iso-paraffins, olefins, naphthenes and compounds greater than C14. The other compounds that are identified in minor amounts

in comparison to iso-paraffins, olefins, naphthenes and compounds greater than C14 are aromatics and paraffins. The DHA analysis of the hydroprocessed product obtained with sulfided CoMo/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst showed an octane value of 71.1.

From the SIMDIS results (**Figure 4**), it can be reported that the OF produced by sulfided CoMo/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> had a boiling temperature range of 156 to 355 °C and contained petroleum equivalents of 85% gasoline (156 °C), 5% jet fuel (180-248 °C) and 5% diesel (248-306 °C) range hydrocarbons. SIMDIS also showed the presence of 5% vacuum gas oil (VGO) range (306- 355 °C) hydrocarbons in the OF.



**Figure 3.** DHA of mass percentage (%) of OF's obtained from sulfided CoMo/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> treatment.



**Figure 4.** Wt% distilled vs boiling temperature (°C) of the sulfided CoMo/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> upgraded liquid fuel determined by SIMDIS.

## V. CONCLUSION

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The comparison of single-stage hydroprocessing using a continuous packed-bed reactor indicates that transportation quality fuels can be produced by this method. Among the tested catalysts sulfided CoMo/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst showed superior activity in terms of OF yield (27.0 wt%) and decreased oxygen content (4 wt%). Compared to raw bio-oil the hydroprocessed product produced by sulfided CoMo/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> contained lower AV, oxygen content and WC and HHV. The DHA of the sulfided CoMo/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst upgraded product predominately contained iso-paraffins, olefins, naphthenes and compounds greater than C14. The other compounds that are identified in minor amounts in comparison to iso-paraffins, olefins, naphthenes and compounds greater than C14 are aromatics and paraffins. The DHA analysis of the hydroprocessed product obtained with sulfided CoMo/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst showed an octane value of 71.1. The OF obtained with sulfided CoMo/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> contained petroleum equivalents of 85% gasoline (156 °C), 5% jet fuel (180-248 °C) and 5% diesel (248-306 °C) range hydrocarbons. SIMDIS also showed the presence of 5% vacuum gas oil (VGO) range (306- 355 °C) hydrocarbons in the fuel.

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## FUTURE STUDY

From our current study, hydroprocessing was performed in a single-stage treatment with RBO over sulfided CoMo/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst. Sulfided CoMo/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst was observed to be superior in performance than reduced catalysts in both properties and yields. Testing of different ranges of operating

conditions to bio-oil in a single stage hydroprocessing method with sulfided CoMo/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst is currently under investigation. Best performing operating conditions will be applied to RBO to perform longer-term deactivation studies to determine the efficacy of the sulfided CoMo/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst in extended runs.

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